



Method Optimization of Deoxyribonucleic Acid (DNA) Thin Films for Biotronics

by Thomas J. Proctor and Amethyst S. Finch

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14. ABSTRACT <p>In today's Army, there is a pressing need to improve the quality of the electronics used in the field. Some requirements include the fabrication of electronic devices that are cheaper, smaller, and lighter, all the while maintaining or even expanding their technical capabilities. An example of this research is the use of deoxyribonucleic acid (DNA) to create thin-film membranes that could be used in electronics. For example, these thin films have been successfully used in light-emitting diodes (LEDs) (1). However, this work focuses on the optimization of membrane fabrication parameters, such as when the sample volume should be added to the spin-coater, spin-coat speed, and solvent type. This can be accomplished by mixing a surfactant, cetyltrimethylammonium chloride (CTAC), with the DNA, causing DNA-cetyltrimethylammonium (DNA-CTMA) to precipitate out of solution. Then, the DNA-CTMA is redissolved in an organic solvent and spin-coated onto a silicon wafer to create the thin film. We demonstrated that certain conditions yield DNA-CTMA films that were thinner and more uniform. We envision that this work could be used in several electronic, photonic, and electro-optic applications.</p>					
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Contents

List of Figures	iv
List of Tables	iv
Acknowledgments	v
1. Introduction	1
2. Experiment	2
2.1 Materials	2
2.2 Thin Film Fabrication.....	2
2.3 Organic Solvent Selection	3
2.4 Sample Volume Selection	3
2.5 Thickness Measurements	4
2.6 Surface Characterization	4
3. Results and Discussion	4
3.1 Acquiring Thickness Data	4
3.2 Sample Volume Added to the Spin-coater	4
3.3 Comparison of Spin-Coating Speed and Sample Volume	5
3.4 Solvent Comparisons.....	6
4. Summary and Conclusions	9
5. References	10
List of Symbols, Abbreviations, and Acronyms	11
Distribution List	12

List of Figures

Figure 1. A comparison of normal LEDs, (top) “Baseline” to the (bottom) DNA improved LEDs “BioLED” (<i>I</i>).	1
Figure 2. Illustration of typical DNA-CTMA precipitate after centrifugation.	3
Figure 3. Diagram of spin-coating method. First, the DNA-CTMA solution was pipetted onto the silicon wafer. Next, the solution was spread out over the wafer due the spinning. Finally, the silicon wafer was set aside to dry.	3
Figure 4. Thickness of the DNA-CTMA films for the various sample volumes at different spin-coating speeds.	6
Figure 5. Thickness of the DNA-CTMA films for the various sample volumes at different spin-coating speeds.	7
Figure 6. Shows a 3-D representation of the surface of the DNA-CTMA film in the ethanol solvent.	8
Figure 7. Shows a 3-D representation of the surface of the DNA-CTMA film in the 1-butanol solvent.	8
Figure 8. Shows a 3-D representation of the surface of the DNA-CTMA film in the isopropanol solvent.	8

List of Tables

Table 1. Sample thickness averaged together and the standard deviations in order to provide a comparison of when the sample volume should be added to the spin-coater.	5
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1. Introduction

In today's technology-driven society, there is a need to improve the qualities of the electronics used. Some requirements are making electronic devices that are cheaper, smaller, and lighter, all while maintaining or even expanding, their technical capabilities. Today's Army has been taking notice of all of these developments with the aim to applying them to the Soldier's heavy and bulky electronics. One solution is to integrate biological material into the electronics. A material being considered for this integration is deoxyribonucleic acid (DNA). DNA is a good possibility because it is cheap, flexible, and lightweight.

One example of this research is using DNA to create thin-film membranes that could eventually be used in electronics. Professor Andrew Steckl of the University of Cincinnati and his co-workers used salmon sperm DNA to make light-emitting diodes (LEDs) brighter and last longer (1). They used DNA-cetyltrimethylammonium (DNA-CTMA) films as an electron blocking layer in both green- and blue-emitting organic LEDs making them bio-organic LEDs. This resulted in 10 times higher efficiency, 30 times brighter output, and 3 times longer lifetime. As shown in figure 1, the LEDs in the top row are the "Baseline" without the DNA-CTMA film as an electron blocking layer and the LEDs in the bottom row have been altered with the DNA-CTMA film as an electron blocking layer.

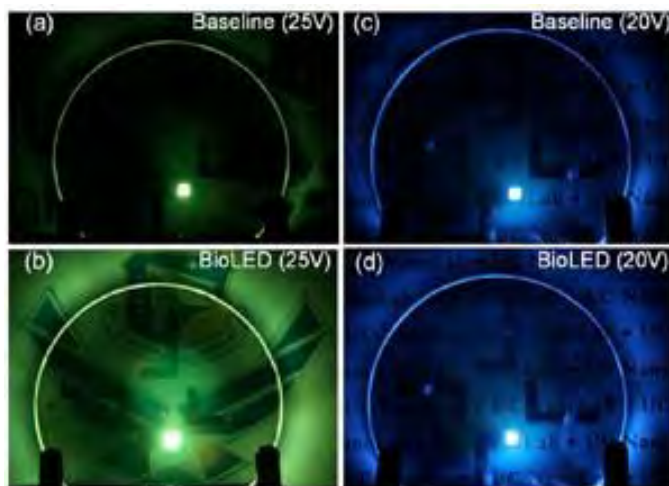


Figure 1. A comparison of normal LEDs, (top) "Baseline" to the (bottom) DNA improved LEDs "BioLED" (1).

Research in the photonics and optoelectronics fields have shown that thin films are necessary for organic electronic devices. They also need to be defect free and provide a surface that will allow for optimal packing of the semiconductor material. The packing efficiency will be affected by the uniformity and is also a function of the surfactant, DNA sequence, length, and molecular weight. Also, it has been shown that the quality of the devices improves when the films are

thinner and more uniform (2). However, this research is mainly focused on the controlled fabrication of films that are more uniform and thinner than the previously reported 200-nm-thick films (2–4). In order to determine the conditions necessary to create similar films, salmon sperm DNA was used for these experiments. This work describes the optimization of parameters including when the sample volume should be added to the spin-coater, sample volume, spin-coat speed, and solvent type. The goal of this work was to improve procedures in order to fabricate uniform and reproducible DNA-CTMA films thinner than previously reported.

2. Experiment

2.1 Materials

All chemicals were purchased from Sigma-Aldrich (St Louis, MO) and were of the highest grade available. Cetyltrimethylammoniumchloride (CTAC) (25 wt. % solution), isopropyl alcohol, 1-butanol (anhydrous, 99.8%), and ethanol (anhydrous, 200 proof, 99.5+%) were used as received. Salmon sperm DNA was purchased from Invitrogen (Carlsbad, CA) with a concentration of 10 mg/mL. Other materials used for the general procedure include a Vortex-Genie 2 (Scientific Industries, Bohemia, New York), a spin-coater (Laurell Technologies, North Wales, PA), sample mounts and silicon wafers (Ted Pella Inc., Redding, CA), an ellipsometer (JA Woollam Co., Lincoln, Nebr), and an atomic force microscope (AFM) (VEECO, Nanoman, Monterey, CA).

2.2 Thin Film Fabrication

First, 10 μ L of salmon sperm DNA, 2 μ L of surfactant (CTAC), and 88 μ L of deionized water were added to 1.5-mL Eppendorf conical polypropylene tubes with snap caps using Eppendorf pipettes, polymerase chain reaction (PCR) clean 10- μ L tips, and PCR clean, dual-filter 200- μ L tips. This solution was vortexed to form a DNA-surfactant complex (DNA-CTMA). Then, the solution was placed into an Eppendorf centrifuge. Running the centrifuge for 6 min at 14000 rpm caused the DNA-CTMA to precipitate out of solution, as seen in the schematic diagram in figure 2. Afterwards, the supernatant was pipetted off using the same pipettes as before with new tips. This was repeated two more times with deionized water to wash the pellet. Next, the precipitate was placed in an Eppendorf vacufuge to vacuum dry for 30 min at 25 °C. The dried DNA-CTMA was then redissolved in an organic solvent. The silicon wafers were then cleaned using the spin-coater by adding 40 μ L of isopropanol to the wafer and spin-coating at 2000 rpm for 60 s.

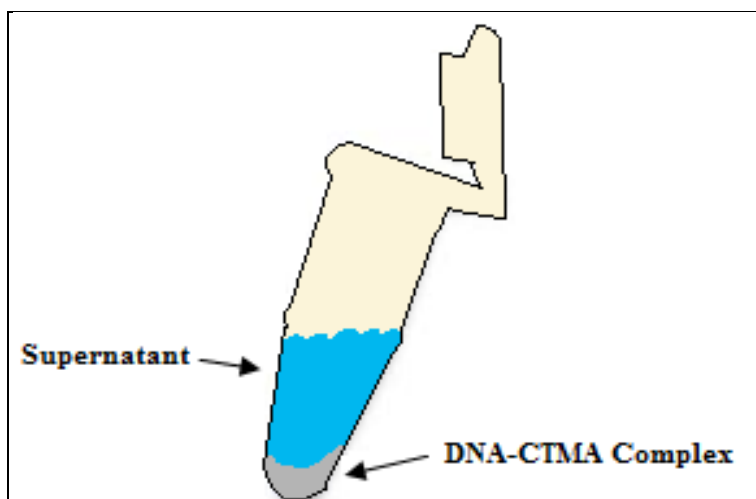


Figure 2. Illustration of typical DNA-CTMA precipitate after centrifugation.

Finally, the redissolved DNA-CTMA solution was spin-coated to the cleaned silicon wafers, as illustrated in figure 3. The volume of solution and revolutions per minute changed based on the test being conducted.

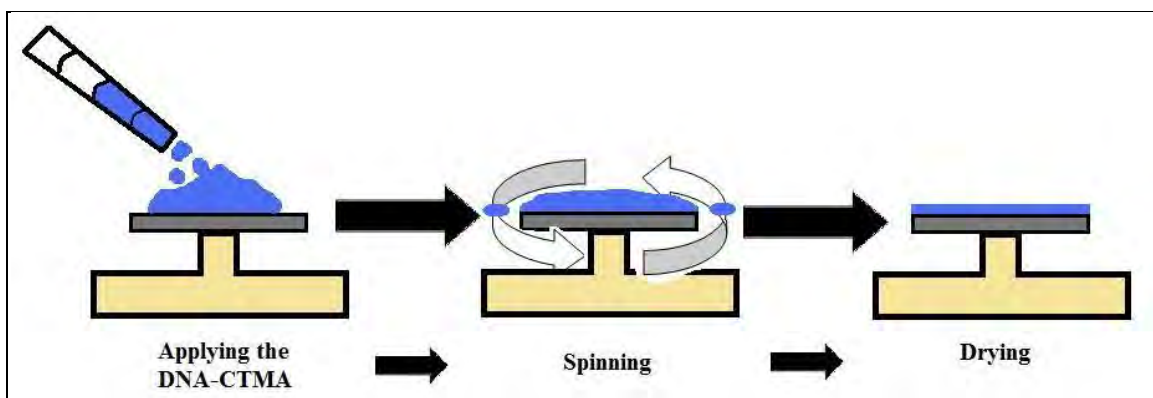


Figure 3. Diagram of spin-coating method. First, the DNA-CTMA solution was pipetted onto the silicon wafer. Next, the solution was spread out over the wafer due the spinning. Finally, the silicon wafer was set aside to dry.

2.3 Organic Solvent Selection

The solvents used in this research were isopropanol, 1-butanol, and ethanol. They were chosen because they are fairly volatile, they leave little or no residue after evaporation, and our sample (DNA-CTMA) is soluble in these solvents.

2.4 Sample Volume Selection

The thickness of a DNA-CTMA film can vary depending on the volume of solution used to coat the silicon wafers. For these experiments, certain volumes of sample solutions were spin-coated for 60 s on each of the silicon wafers. These volumes were 20, 20-20, 20-20-20, and 40 μL . In order to properly cover the wafers, the 20-20 and 20-20-20 μL volumes were completed in

phases. In other words, 20 μL of solution were added, spin-coated then dried prior to adding the next layer. The 20- μL volume gave the opportunity to witness what a relatively small volume would be able to cover. While the 40- μL volume provided the opposite effect of having a large quantity to cover the silicon wafers.

2.5 Thickness Measurements

The ellipsometer (JA Woollam Co., Lincoln, NE) was used for determining the thickness of DNA-CTMA layer on the silicon (Si) wafer. The thickness of the DNA-CTMA layer was calculated by using models with a 1-mm Si layer and a silicon dioxide (SiO_2) layer of approximately 26 Å. Five measurements were taken on the wafer in different locations. The first was in the middle and the other four were near the corners of the silicon wafer. After these measurements were taken, they were averaged together to conclude a thickness with the standard deviation between the data points.

2.6 Surface Characterization

Also, the surface topography of the wafers was examined using an AFM in tapping mode. First, the tips used in the AFM were changed to a Veeco (VEECO, Nanoman, Monterey, CA) tapping mode tip (model: OTESPA). Then, the laser was placed on the tip. Next, the video crosshairs were moved to locate the tip. After that the sample was placed on the stage, the tip reflection and surface images were focused. Then, the meter dot was adjusted to 0 V. Afterward, the tip was auto-tuned. The parameters were then set to a scan size of 0.5 to 1 μm , a scan rate of 0.501 Hz, 256 samples per line, 256 lines, and the data type in height. Next, the tip was engaged. Once engaged, the integral gain and proportional gain were adjusted to give good tracking for the scan. Three or four scans were captured per sample. One scan was near the middle of the sample and the others were taken about halfway between the middle and the edge.

3. Results and Discussion

3.1 Acquiring Thickness Data

The primary tool used to collect data for these experiments was the ellipsometer. The ellipsometer measures the change of light upon reflection of the sample. The change in the light is determined by the sample's thickness. A new model for the ellipsometry was created for each set of samples. The main difference in the models was that the thickness of the SiO_2 layer would vary on the blank Si wafers.

3.2 Sample Volume Added to the Spin-coater

First, we examined whether it was more beneficial to add the samples to the Si wafers before spinning or while spinning. This was tested by selecting two different volumes, 40 and 20-20 μL , of the DNA-CTMA samples to be applied. The 40- μL volume was selected because

the large quantity would have a greater impact in difference of coverage on the wafers. The 20-20 μL volume was chosen to view the effects of the spinning during the multiple applications. The comparison done between the two volumes of sample was measured by having samples added to four Si wafers before the spinning would begin and four Si wafers while the wafers were spinning. In each case, two wafers were for the 20-20 μL sample and two wafers were for the 40- μL sample. All samples were run for 60 s at 2000 rpm. Table 1 shows the thickness, determined by using ellipsometry, of the DNA-CTMA films prepared using the different spin-coating methods.

Table 1. Sample thickness averaged together and the standard deviations in order to provide a comparison of when the sample volume should be added to the spin-coater.

Before Spinning	Thickness (Å)	vs.	Thickness (Å)	While Spinning
B1-20-20	223.03		292.69	W1-20-20
B2-20-20	240.42		286.93	W2-20-20
Average	231.725		289.81	Average
Standard deviation	10.75		13.75	Standard deviation
B1-40	179.67		188.3	W1-40
B2-40	177.1		193.16	W2-40
Average	178.385		190.73	Average
Standard deviation	4.43		8.11	Standard deviation

All of the samples that were added to the Si wafer before spinning were thinner than the samples prepared by adding DNA-CTMA while spinning. Also, the standard deviation of thickness was smaller for the “before spinning” samples, indicating that this method is more reproducible.

3.3 Comparison of Spin-Coating Speed and Sample Volume

Next, we determined the optimal spin-coating speed and sample volume used to fabricate spin-coated DNA-CTMA films. All four sample volume variations were used in this experiment. The samples were spin-coated for 60 s at five different speeds: 500, 1000, 2000, 3000, and 4000 rpm. Figure 4 shows film thicknesses, determined by the ellipsometry measurements, of DNA-CTMA films prepared at five different spin-coating speeds. The thickness of the films decreased overall as spin-coating speed increased, but the different volumes of DNA-CTMA solution behaved differently.

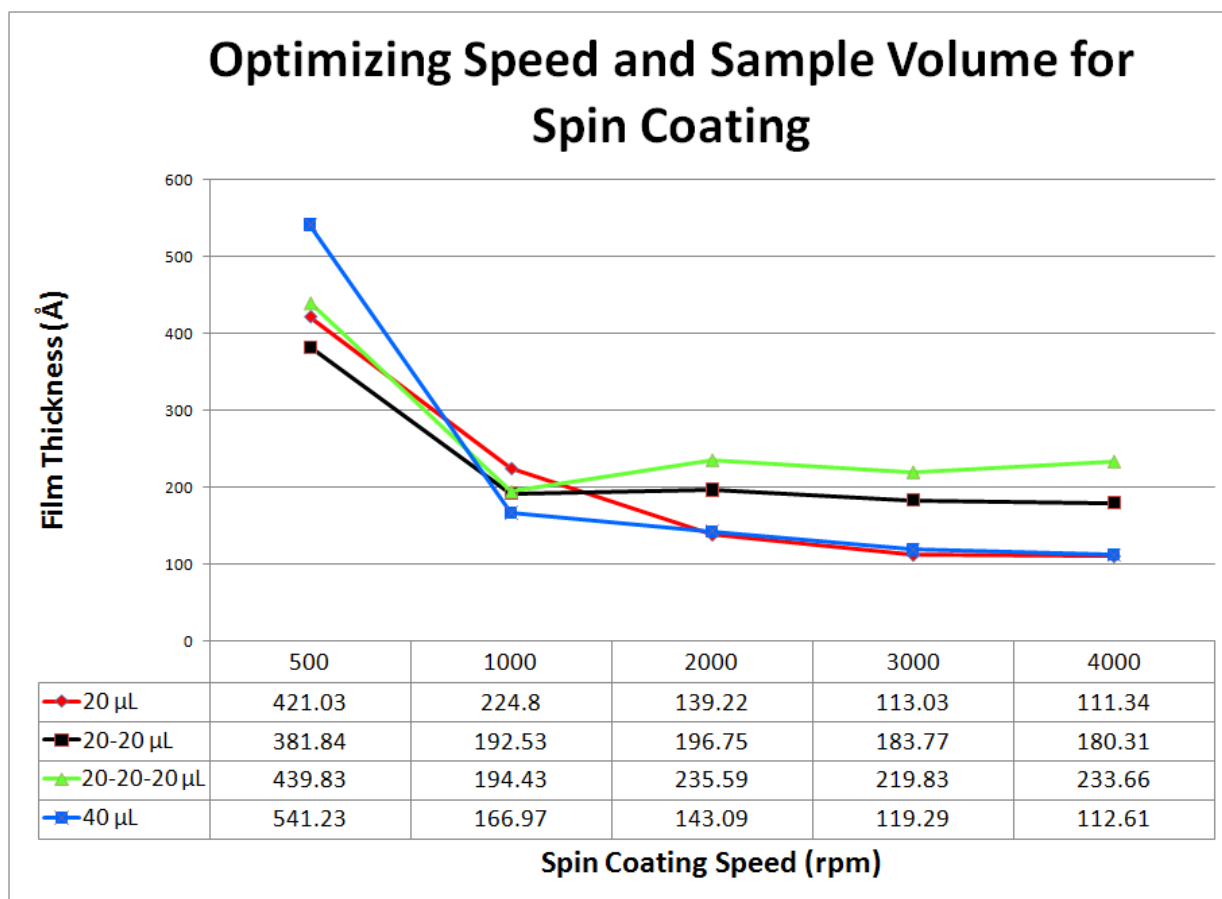


Figure 4. Thickness of the DNA-CTMA films for the various sample volumes at different spin-coating speeds.

The thickness of films prepared from 20- μ L volume had a negative trend as spin-coating speed increased. The 20-20 μ L samples also had a negative trend in thickness between 500 and 1000 rpm but then leveled off at higher speeds. The 20-20-20 μ L samples had a negative trend in thickness to 2000 rpm, but showed a slight increase in thickness to 4000 rpm. The 40- μ L DNA-CTMA sample showed a rapid decrease in film thickness between 500 and 1000 rpm, but then leveled off with a slight decrease across the other speeds. Even though the various volumes of sample behaved differently, at 4000 rpm, three out of the four samples gave a standard deviation less than 3Å between the five thickness measurements, indicating that this spin-coating speed yielded more uniform films.

3.4 Solvent Comparisons

Next, we compared three solvents used to dissolve DNA-CTMA. The solvent comparison was used to determine if another solvent was better than isopropanol to redissolve the DNA-CTMA. Therefore, an assessment was made to compare ethanol, 1-butanol, and isopropanol. This time only the 40- μ L volumes were used. The 40- μ L volume was chosen, because its film would be thinner at higher spin-coating speeds than the other sample volumes. This volume was also spin-coated at various speeds: 2500, 3000, and 4000 rpm.

Figure 5 shows the thickness, established by ellipsometry, of the DNA-CTMA films for the various solvents tested. Dissolving DNA-CTMA in isopropanol or ethanol gives similar trends. Both thicknesses decreased from 60 and 130 Å at 2500 rpm to 51 and 78 Å at 3000 rpm. The thicknesses increased slightly from 3000 to 4000 rpm. Although the trend in thickness was comparable, the thicknesses themselves were significantly different. 1-Butanol acted the complete opposite of the other two solvents. The thickness of the DNA-CTMA films increased from 31.17 Å at 2500 rpm to 54.31 Å at 3000 rpm and slightly decreased to 49.41 Å at 4000 rpm. Dispersions in 1-butanol and isopropanol produce considerably thinner films compared to the ethanol solvent. These dispersions cause the DNA-CTMA to spread out, giving a thinner film. Also, 1-butanol has the highest boiling point (82.4 °C) of the three alcohol solvents; it produced the most uniform films. This means that the choice of solvent does have an impact on the thickness and uniformity of the DNA-CTMA films. 1-Butanol produced better films, because the films were thinner and more uniform than previously recorded.

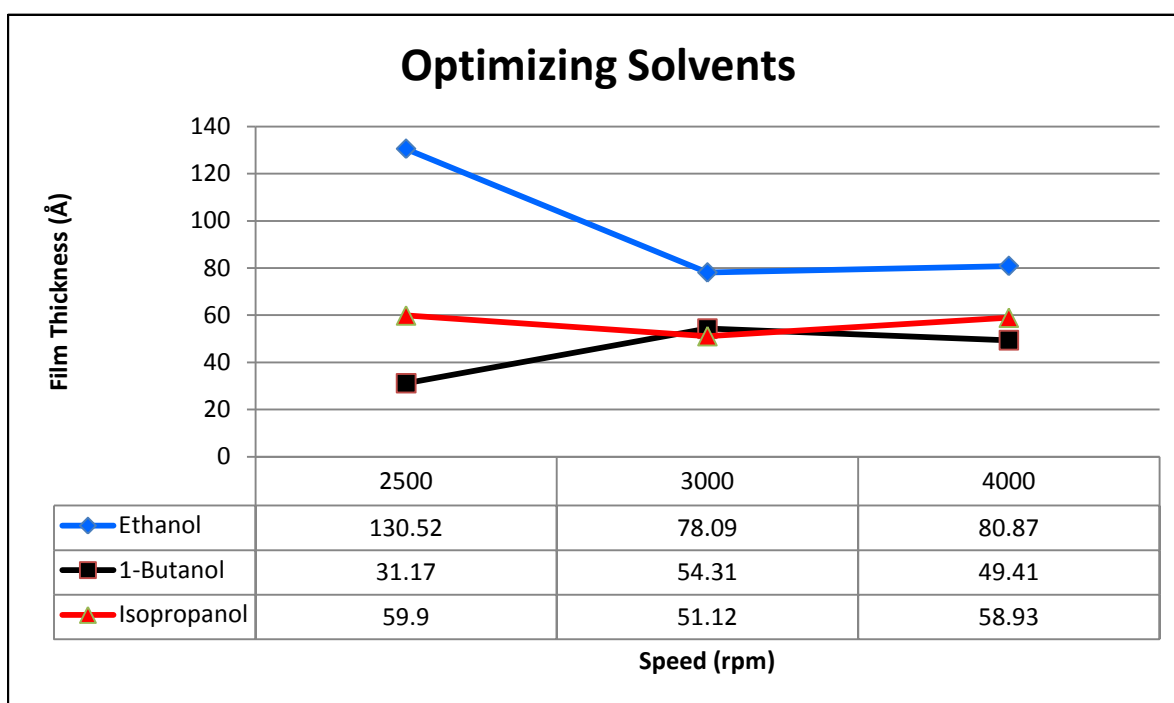


Figure 5. Thickness of the DNA-CTMA films for the various sample volumes at different spin-coating speeds.

Figures 6 through 8 are three-dimensional (3-D) representations of the DNA-CTMA film surfaces from the samples spin-coated at 4000 rpm.

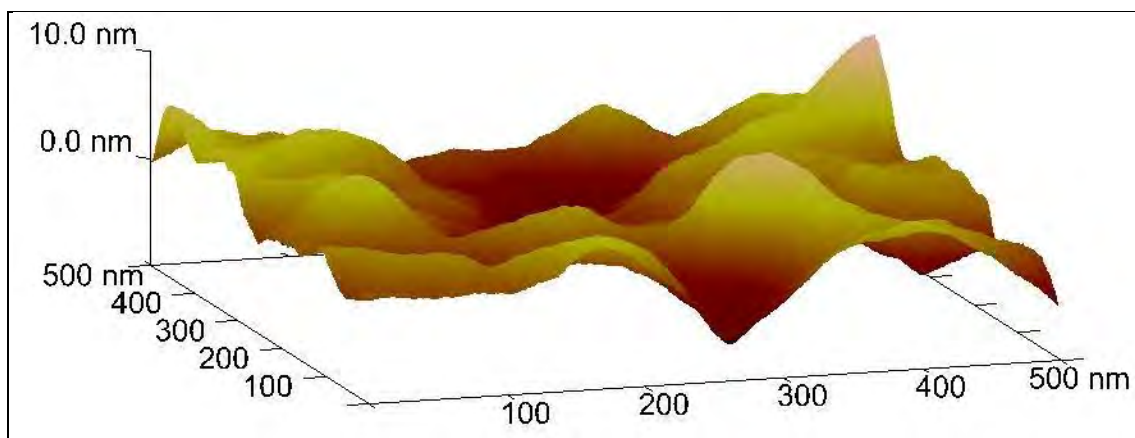


Figure 6. Shows a 3-D representation of the surface of the DNA-CTMA film in the ethanol solvent.

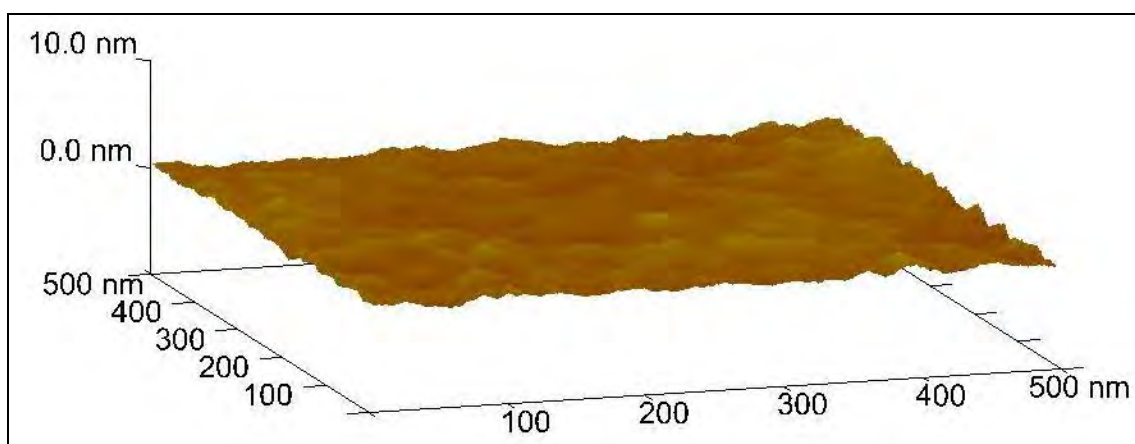


Figure 7. Shows a 3-D representation of the surface of the DNA-CTMA film in the 1-butanol solvent.

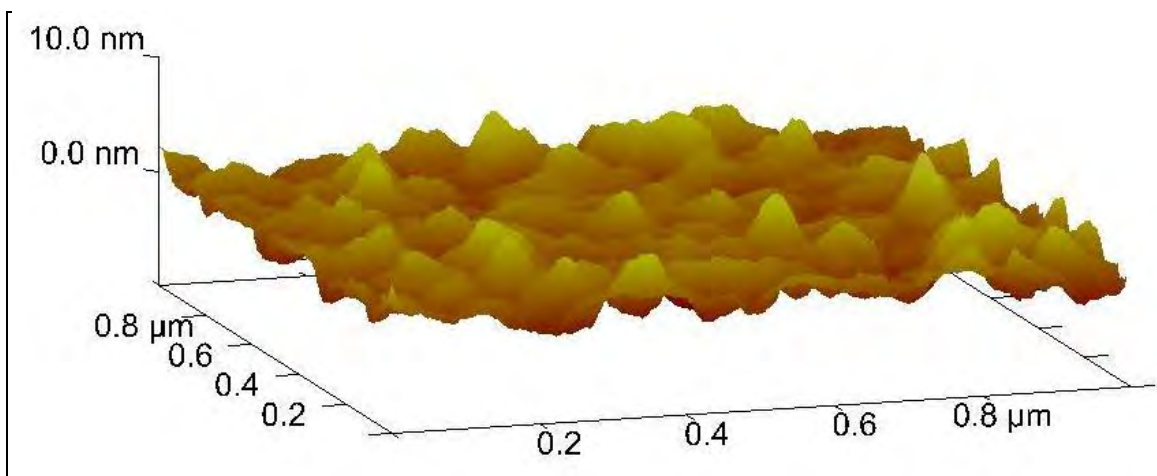


Figure 8. Shows a 3-D representation of the surface of the DNA-CTMA film in the isopropanol solvent.

4. Summary and Conclusions

The results of these three studies were used to determine the optimal fabrication conditions for DNA-CTMA thin films. Because of the low average thickness and low standard deviation, placing the sample on the Si wafers before spinning should work better. The results showed that this method produced a reproducible, more uniform film. The 40- μ L volume showed that even at lower spin-coating speeds it had the ability to produce a thinner film. Also, a spin-coating speed of 4000 rpm should be used, because it allows the film to be thinner across the Si wafer. 1-Butanol should be the solvent used due to better uniformity.

In conclusion, there are a variety of factors that can affect the thickness and uniformity of DNA-CTMA films. This project focused on controlling and optimizing these aspects, such as when the sample volume should be added to the spin-coater, sample volume, spin-coat speed, and solvent type. This work showed that some choices are better than others with regard to these factors. However, more work can and should be done. Future work should include the examination of different types of DNA beyond salmon sperm, DNA sequence, length, and molecular weight. This work will be useful in the preparation of thin films for several electronic and electro-optic applications.

5. References

1. Hagen, Joshua A.; Grote, James G.; Li, Wayne X.; Steckl, Andrew J.; Diggs, Darnell E.; Zetts, John S.; Nelson, Robert L.; Hopkins, F. K. Organic Light Emitting Diode with a DNA Biopolymer Electron Blocking Layer. *Proc. SPIE 6333* **2006**, 63330J, doi:10.1117/12.682251.
2. Heckman, E. M.; Hagen, J. A.; Yaney, P.; Grote, J. G.; Hopkins, F. K. *Appl. Phys. Lett.* **2005**, *87*, 211115.
3. Singh, B.; Sarcift ci, N. S.; Grote, J. G.; Hopkins, F. K. *J. Appl. Phys.* **2006**, *100*, 024514.
4. Singh, B.; Sarcift ci, N. S.; Grote, J. G. Bio-organic Optoelectronic Devices Using DNA. *Adv. Polym. Sci.* **2009**, doi:10.1007/12_2009_6.

List of Symbols, Abbreviations, and Acronyms

AFM	atomic force microscope
CTAC	cetyltrimethylammoniumchloride
DNA	deoxyribonucleic acid
DNA-CTMA	DNA-cetyltrimethylammonium
LEDs	light-emitting diodes
PCR	polymerase chain reaction
Si	silicon
SiO ₂	silicon dioxide

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